# V.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

## ON SUBSTITUTED PYROMUCIC ACIDS.

### FIRST PAPER.

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### ON BROMPYROMUCIC ACIDS.

ALTHOUGH pyromucic acid has long been known and has been made the subject of many investigations, its behavior toward the halogens has been studied by but few chemists. As early as 1837 Malaguti * showed that ethyl pyromucate, when treated with dry chlorine, took up four atoms of chlorine forming the ethyl ether of pyromucic tetrachloride. This ether he treated with potassic hydrate, but isolated no product resulting from this decomposition. In 1865 Schmelz and Beilstein † studied the action of aqueous chlorine and bromine upon the acid, and described the resulting four-carbon compounds mucochloric and mucobromic acids. A few years later Limpricht,‡ with several of his pupils, pursued the subject further in the same direction, and isolated, among the products formed by the action of bromine and water upon pyromucic acid, fumaric acid, and its half aldehyde; they made, however, no experiments concerning the action of dry bromine. Toennies,§ working in Baeyer's laboratory, in 1878, prepared the pyromucic tetrabromide by the action of dry bromine upon pyromucic acid, and found that it could be converted into a dibrompyromucic acid melting at 184–186° by the action of alcoholic potash. Toennies did not publish, however, any very extended description of this acid, although he mentions its stability in resisting the action of various oxidizing

* Ann. Chim. Phys., lxiv. 282; lxx. 371.
† Ann. Chem. u. Pharm., Suppl., iii. 276.
‡ Ann. Chem. u. Pharm., clxv. 253.
§ Berichte d. deutsch. chem. Gesellsch., xi. 1086; xii. 1203.

agents, and describes a derivative resulting from the action of bromine water, to which he gives the formula $C_4H_2Br_2O_2$. By heating the pyromucic tetrabromide he also obtained an acid melting at 180°, to which he assigned no formula, but which from his analyses was evidently a monobrompyromucic acid.

About the time of Toennies's first publication, Schiff and Tassinari [*] described two acids which they had obtained by allowing one molecule of bromine to act upon ethyl pyromucate, and decomposing the product thus obtained by alcoholic potash. These acids contained but one atom of bromine, one melted at 180° the other at 157°, and they were named by Schiff and Tassinari the $\alpha$ and $\beta$ monobrompyromucic acids. The only statement which they make, beyond a mere description of the physical properties of the two acids, is that one acid may be converted into the other by continued boiling with concentrated hydrochloric acid. This change they consider analogous to the conversion of $\beta$-bromcinnamic acid into $\alpha$-bromcinnamic acid under similar circumstances, and following this analogy they assign to the two acids the formulæ

In a paper published rather more than a year after the appearance of a preliminary note upon this subject by one of us,[†] Canzoneri and Oliveri,[‡] without in any way alluding to this previous publication, described certain salts of the dibrompyromucic acid of Toennies and of one of the monobrompyromucic acids of Schiff and Tassinari, while they showed that the isomeric acid melting at 157° had no real existence. Our own experiments had already led us to the same conclusion.

Since of the various acids which could be formed by the replacement of the hydrogen atoms of pyromucic acid by halogens at most but three had been prepared, and none of these had been studied in any detail, we undertook the preparation and study of the brompyromucic acids. In the preparation of pyromucic tetrabromide, which first attracted our attention, we found it impossible to prevent completely the evolution of hydrobromic acid. Since Toennies's analysis of a product

* Berichte d. deutsch. chem. Gesellsch., xi. 842; Gazzetta Chimica, viii. 297.
† Berichte d. deutsch. chem. Gesellsch., xvi. 1130.
‡ Gazzetta Chimica, xiv. 173.

formed by heating the tetrabromide had shown that a monobrompyromucic acid could thus be formed, we attempted to prepare it by heating the tetrabromide carefully in an oil bath. Although bromine was set free together with hydrobromic acid and monobrompyromucic acid was formed, we did not succeed in making the reaction available for the preparation of this acid on a larger scale. If, on the other hand, the bromine was allowed to act upon the pyromucic acid at the outset at higher temperature, there was little difficulty in securing abundant substitution and excellent product. At first we used glacial acetic acid as a solvent to facilitate the reaction, but we afterwards found that we could easily dispense with it, and that we could at our pleasure replace one or two hydrogen atoms in the pyromucic acid by bromine by varying the conditions of the reaction. The monobrompyromucic acid formed in this way melted at 183–184°, and appeared to be identical with that already described by Schiff and Tassinari, as far as could be judged from their meagre description, while the dibrompyromucic acid was new and melted at 167–168°.

In studying the action of alkalies upon the pyromucic tetrabromide, we found that the product formed was a mixture of two isomeric dibrompyromucic acids, one of which was identical with that formed by the direct action of bromine upon pyromucic acid, while the second melted at 190–191°, and was presumably identical with that which Toennies had prepared in the same way, although he had not obtained it in a state of perfect purity. While we have been wholly unable to verify the assertion of Schiff and Tassinari, that a monobrompyromucic acid exists, whose melting-point is 157°, we have found that a new monobrompyromucic acid melting at 128–129° can be made by the reduction of either of the two dibrompyromucic acids. We have also found it a matter of no difficulty to prepare tribrompyromucic acid, either by direct substitution from one of the dibrompyromucic acids, or by decomposing with alkalies the monobrompyromucic tetrabromide.

These various substituted pyromucic acids are in many respects more stable than pyromucic acid itself, and we have been able to determine the relative position of the several bromine atoms through a study of their oxidation products.

### δ-Monobrompyromucic Acid.

Bromine acts upon pyromucic acid readily at 100° and forms a monobrompyromucic acid. To insure a satisfactory yield we have

found it necessary to add the bromine slowly, and to take care that no liquid bromine comes in contact with the pyromucic acid. We have accomplished this very conveniently by hanging inside the flask containing the pyromucic acid a small glass cup, so arranged as to catch the liquid dropping from the reverse cooler and drop-funnel with which the flask is fitted. If the flow of the bromine be carefully regulated and the flask heated in a water bath, the process requires little attention. The reaction, however, is not perfectly smooth. Carbonic dioxide is evolved, and, as more or less bromine is unavoidably lost with the escaping hydrobromic acid, considerably more than one molecule of bromine must be added to insure the best result. For 20 grammes of pyromucic acid we have found it best to use 36 grammes of bromine instead of the 28.57 grammes required by theory. When the reaction is over, the product is dissolved in hot water, filtered, and the voluminous leafy crystals which separate on cooling are purified by recrystallization from hot water. If the bromine has not been added with due care the product may contain more or less dibrompyromucic acid, and is deposited then on cooling the hot aqueous solution in fine granular crystals. The dibrompyromucic acid may, however, readily be removed by precipitating an ammoniacal solution with baric chloride and acidifying the filtered solution with hydrochloric acid. We have not succeeded in obtaining perfectly uniform results in the preparation of the acid, and the yield of pure product has varied between 40 and 60 per cent of the theoretical amount. While we have been unable to prove that isomeric monobrompyromucic acids are formed in the reaction, the properties of the $\beta$-monobrompyromucic acid subsequently described are such that a small quantity of it, if formed, might easily escape detection.

The acid crystallized from hot water and dried over sulphuric acid gave on analysis the following results: —

I. 0.2291 grm. substance gave 0.2629 grm. $CO_2$ and 0.0322 grm. $H_2O$.
II. 0.2571 grm. substance gave 0.2959 grm. $CO_2$ and 0.0400 grm. $H_2O$.
III. 0.1944 grm. substance gave 0.1912 grm. AgBr.
IV. 0.1993 grm. substance gave 0.1957 grm. AgBr.
V. 0.2085 grm. substance gave 0.2051 grm. AgBr.

| | Calculated for $C_5H_3BrO_3$. | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| C | 31.42 | 31.30 | 31.38 | | | |
| H | 1.57 | 1.56 | 1.73 | | | |
| Br | 41.89 | | | 41.85 | 41.78 | 41.86 |

The δ-monobrompyromucic acid crystallizes from water in irregular leafy plates with pearly lustre which melt at 183–184°. It is readily soluble in alcohol or ether, sparingly soluble in cold chloroform or benzol, more freely soluble on heating. In carbonic disulphide or ligroin it is almost insoluble. In cold water it is sparingly soluble, but dissolves freely on heating. The solubility of the acid in water at ordinary temperatures we determined according to the method of V. Meyer. The acid solution was neutralized with baric carbonate and the barium dissolved precipitated with sulphuric acid.

I. 37.5965 grm. of a solution saturated at 16.5° gave 0.0500 grm. $BaSO_4$.
II. 36.6804 grm. of a solution saturated at 16.5° gave 0.0488 grm. $BaSO_4$.

The aqueous solution of the acid saturated at 16.5° therefore contained the percentages: —

| I. | II. |
|---|---|
| 0.22 | 0.22 |

*Baric δ-Monobrompyromucate*, $Ba(C_5H_2BrO_3)_2 \cdot 4\,H_2O$. — By neutralizing an aqueous solution of the acid with baric carbonate we obtained the barium salt in the form of irregular pearly plates which were readily soluble in hot water, more sparingly in cold. The air-dried salt contained four molecules of water,* most of which it lost over sulphuric acid.

I. 1.2927 grm. of the salt lost at 105° 0.1563 grm. $H_2O$.
II. 1.3857 grm. of the salt lost at 105° 0.1676 grm. $H_2O$.

| | Calculated for $Ba(C_5H_2BrO_3)_2 \cdot 4\,H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 12.23 | 12.09 | 12.10 |

I. 0.3394 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1527 grm. $BaSO_4$.
II. 0.4088 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1848 grm. $BaSO_4$.

| | Calculated for $Ba(C_5H_2BrO_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ba | 26.50 | 26.44 | 26.57 |

* Canzoneri and Oliveri assign to this salt the formula $Ba(C_5H_2BrO_3)_2 \cdot 2\frac{1}{2}H_2O$. Since their analytical data agree with ours, their incorrect formula is evidently due to an error in calculation.

The solubility of the salt in water at ordinary temperatures we also determined.

I. 8.1035 grm. of a solution saturated at 18° gave on precipitation with $H_2SO_4$ 0.1226 grm. $BaSO_4$.
II. 7.3943 grm. of a solution saturated at 18° gave on precipitation with $H_2SO_4$ 0.1122 grm. $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 3.36 | 3.37 |

*Calcic δ-Monobrompyromucate*, $Ca(C_5H_2BrO_3)_2 . 3\,H_2O$. — The calcium salt prepared by neutralizing an aqueous solution with calcic carbonate formed small prisms clustered in globular aggregations which were sparingly soluble in cold water, somewhat more readily in hot.

I. 1.4814 grm. of the air-dried salt lost at 100° 0.1682 grm. $H_2O$.
II. 3.1181 grm. of the air-dried salt lost at 100° 0.3534 grm. $H_2O$.
III. 0.2135 grm. of the air-dried salt gave on ignition with $H_2SO_4$ 0.0614 grm. $CaSO_4$.

| | Calculated for $Ca(C_5H_2BrO_3)_2 . 3\,H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| $H_2O$ | 11.40 | 11.35 | 11.33 | |
| Ca | 8.44 | | | 8.47 |

I. 0.3175 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1032 grm. $CaSO_4$.
II. 0.3939 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1281 grm. $CaSO_4$.

| | Calculated for $Ca(C_5H_2BrO_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ca | 9.53 | 9.56 | 9.57 |

The solubility of the calcium salt in water we determined by precipitating with ammonic oxalate the solution prepared according to the method of V. Meyer, and converting the calcic oxalate thus obtained into sulphate by ignition with sulphuric acid.

I. 17.9259 grm. of a solution saturated at 20° gave 0.0620 grm. $CaSO_4$.
II. 15.5795 grm. of a solution saturated at 20° gave 0.0528 grm. $CaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 1.07 | 1.05 |

*Argentic δ-Monobrompyromucate*, $AgC_5H_2BrO_3$. — The silver salt falls as a crystalline precipitate on the addition of argentic nitrate to an aqueous solution of the free acid. We prepared it, however, by precipitating a solution of the potassium salt with argentic nitrate, and recrystallized the product from boiling water. It formed small clustered plates sparingly soluble even in boiling water, which could be recrystallized without decomposition from hot water.

0.2321 grm. of the salt dried over sulphuric acid gave on precipitation with HBr 0.1465 grm. AgBr.

| | Calculated for $AgC_5H_2BrO_3$. | Found. |
|---|---|---|
| Ag | 36.24 | 36.25 |

*Sodic δ-Monobrompyromucate*, $NaC_5H_2BrO_3$. — On neutralizing the acid with sodic carbonate we obtained the sodium salt in the form of small radiated needles which proved to be anhydrous.

I. 0.4172 grm. of the salt gave on ignition with $H_2SO_4$ 0.1388 grm. $Na_2SO_4$.

II. 0.6014 grm. of the salt gave on ignition with $H_2SO_4$ 0.1993 grm. $Na_2SO_4$.

| | Calculated for $NaC_5H_2BrO_3$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Na | 10.80 | 10.78 | 10.74 |

*Potassic δ-Monobrompyromucate*, $KC_5H_2BrO_3$. — The potassium salt crystallized in irregular flattened prisms which were very soluble in water, and contained no water of crystallization.

I. 0.3118 grm. of the salt gave on ignition with $H_2SO_4$ 0.1191 grm. $K_2SO_4$.

II. 0.3384 grm. of the salt gave on ignition with $H_2SO_4$ 0.1285 grm. $K_2SO_4$.

| | Calculated for $KC_5H_2BrO_3$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| K | 17.07 | 17.15 | 17.05 |

*Ethyl δ-Monobrompyromucate*, $(C_2H_5)C_5H_2BrO_3$. — The ethyl ether of the acid can readily be made by heating the acid with absolute alcohol and concentrated sulphuric acid, or by the action of ethyl iodide upon the silver salt * It may conveniently be prepared by warming for several hours on the water bath a mixture of four parts of absolute alcohol and three parts of concentrated sulphuric acid with four parts of the acid. A portion of the ether separates while the mixture is still hot, and on cooling and precipitating with water the quantity of ether obtained is nearly equal to that of the acid taken. The ether, washed with a dilute solution of sodic carbonate, and dried with calcic chloride, had a fragrant odor resembling ethyl pyromucate, and boiled between 234.5° and 236.5°, the greater portion showing a constant boiling-point of 235° † (mercury column completely in vapor) under a pressure of 767 mm. Since it retained a slight

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* We attempted at first to prepare this ether by saturating the alcoholic solution of the acid with hydrochloric acid gas. The product which we thus obtained boiled at 132° under a pressure of 20 mm., and showed no signs of crystallization when strongly cooled. An analysis showed that this product contained much too high a percentage of halogen, and the results agreed quite closely with those required by the formula $(C_2H_5)C_5H_4BrCl_2O_3$.

| | Calculated for $(C_2H_5)C_5H_4BrCl_2O_3$. | Found. | |
|---|---|---|---|
| $BrCl_2$ | 51.71 | 51.84 | 52.28 |

This behavior of the acid requires further investigation.

† The thermometer used was a "Zincke" thermometer made by Geissler. It gave the boiling-point of pure naphthaline under a pressure of 769 mm. with the mercury column completely in vapor as 217.6°. According to Crafts (Am. Journal Chemistry, v. 324) this boiling-point is about one degree too low, although it agrees exactly with that taken by Geissler in the graduation of his thermometers. Several years ago I gave the boiling-point of a specimen of ethyl pyromucate prepared by Mr. J. J. Thomsen as 195° under a pressure of 766 mm. (these Proceedings, vol. xvi. (N. S. viii.) p. 160), this boiling-point being materially lower than that given by Malaguti (Ann. Chim. Phys., [2,] lxiv. 279), 208–210°, under a pressure of 756 mm. Since Canzoneri and Oliveri have recently given the boiling-point of the ether as 205–208°, I have thought it worth while to repeat the determination. The thermometer I had previously used was made by Geissler, but I had neglected to determine its correctness above 200° by means of the boiling-point of naphthaline. An entirely different preparation of the ether, which melted at 34–35° (somewhat higher than the old preparation), showed with the above "Zincke" thermometer the constant boiling-point 195° under a pressure of 769 mm., the mercury column being completely in the vapor. The ether was then allowed to stand for eighteen hours with fused calcic chloride, the temperature being for a great part of the time just above the melting-point of the ether. The boiling-point was still found to be constant at 195° under a pressure of 768 mm.

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yellowish tinge after several distillations, we distilled it for analysis under diminished pressure, and found it to boil at 133–134° under a pressure of 31 mm. On cooling, the ether crystallized in clear prisms with bevelled ends. The melting-point of the solidified ether was found to be 17°, and when the liquid ether was cooled to 13°, and a crystal of the solid ether introduced, the thermometer rose to 17°. The specific gravity of the ether at 20° referred to water at the same temperature we found to be 1.528.

Analyses I. and II. were made with substance prepared from the silver salt; III. and IV. from substance made with sulphuric acid.

I. 0.2171 grm. substance gave 0.1875 grm. AgBr.
II. 0.1616 grm. substance gave 0.1380 grm. AgBr.
III. 0.3571 grm. substance gave 0.3042 grm. AgBr.
IV. 0.3080 grm. substance gave 0.2623 grm. AgBr.

| | Calculated for $(C_2H_5)C_5H_2BrO_3$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Br | 36.52 | 36.76 | 36.35 | 36.25 | 36.23 |

*δ-Monobrompyromucamide*, $C_5H_2BrO_2NH_2$. — Concentrated aqueous ammonia acts but slowly upon the ether in the cold, and several days are necessary to complete the reaction. At 100° in a sealed tube the decomposition is perfect in a few hours, but the yield of the amide is apparently not so satisfactory. The product of the reaction when recrystallized from boiling water forms long shining needles which melt at 144–145°. They are sparingly soluble in cold water, readily in hot, readily soluble in alcohol, ether, chloroform, or in hot benzol, sparingly soluble in cold benzol or carbonic disulphide. For analysis the substance was recrystallized from boiling water and dried over sulphuric acid.

0.7761 grm. substance gave 50.6 c.c. of moist nitrogen at 20°, and under a pressure of 747 mm.

| | Calculated for $C_5H_2BrO_2NH_2$. | Found. |
|---|---|---|
| N | 7.37 | 7.46 |

*δ-Monobrompyromucic tetrabromide.* — When exposed to an atmosphere of bromine, the δ-monobrompyromucic acid takes up four atoms of bromine. The addition product is readily soluble in alcohol or ether, is decomposed by water, but may be recrystallized from glacial acetic acid. It forms fine needles which decompose without melting at 173°.

0.1948 grm. substance gave 0.3594 grm. AgBr.

| | Calculated for $C_5H_3Br_5O_3$. | Found. |
|---|---|---|
| Br | 78.29 | 78.52 |

*Action of Bromine and Water.*

Since pyromucic acid itself is readily attacked by aqueous bromine, and converted, according to the conditions of the reaction, into fumaric aldehyd or mucobromic acid, it seemed to us of interest to study the behavior of the $\delta$-monobrompyromucic acid under similar conditions. We have found that the products formed vary greatly according to the conditions chosen, but in every case they prove to contain but four carbon atoms.

The acid was suspended in about thirty times its weight of cold water, and the vapor of bromine slowly led in by means of a current of air. Two molecules of bromine were found necessary to complete the reaction. The strongly acid solution, when extracted repeatedly with ether, gave an acid sparingly soluble in cold water, more readily in hot, which, when recrystallized from hot water, proved to be free from bromine. The behavior of this acid on heating showed it to be fumaric acid. Its identity was further established by an analysis of the silver salt.

0.5462 grm. of the salt gave 0.6194 grm. AgBr.

| | Calculated for $Ag_2C_4H_2O_4$. | Found. |
|---|---|---|
| Ag | 65.46 | 65.13 |

Beside the fumaric acid could be isolated minute quantities of two acids which contained bromine, and which from their physical properties appeared to be dibromsuccinic and isodibromsuccinic acids. These acids were formed in much larger quantity when the bromine was rapidly added; considerably more than two molecules of bromine were required to complete the reaction, and at the same time a crystalline substance insoluble in water was then formed. The aqueous solution was filtered from this insoluble substance and extracted with ether. The ethereal extract upon evaporation left a white crystalline residue which contained but little fumaric acid, and proved to consist mainly of about equal quantities of two acids, which could be separated by repeated recrystallization from water. The more soluble acid could be obtained by slow evaporation in well-formed rhombic plates which melted at 165°, and which on analysis proved to contain the percentage of bromine required by isodibromsuccinic acid.

I. 0.2434 grm. of substance gave 0 3344 grm. AgBr.
II. 0.2427 grm. of substance gave 0.3305 grm. AgBr.

| | Calculated for $C_4H_4Br_2O_4$. | Found. I. | Found. II. |
|---|---|---|---|
| Br | 57.97 | 58.44 | 57.94 |

The less soluble acid crystallized from hot water in well-defined prisms, which remained unchanged when heated to 200°. An analysis showed this acid to be ordinary dibromsuccinic acid.

0.2468 grm. substance gave 0.3363 grm. AgBr.

| | Calculated for $C_4H_4Br_2O_4$. | Found. |
|---|---|---|
| Br | 57.97 | 57.98 |

The aqueous solution from which the two dibromsuccinic acids had been extracted with ether still contained a certain amount of fumaric acid, which was obtained by evaporation and identified by qualitative tests.

The substance insoluble in water which had been formed by the action of bromine was recrystallized, first from alcohol, then from ligroin, and crystallized in colorless prisms which melted at 110–111°. Analysis showed the substance to be dibromfurfurantetrabromide.

I. 0.7407 grm. substance gave 0.2380 grm. $CO_2$ and 0.0284 grm. $H_2O$.
II. 0.2054 grm. substance gave 0.4259 grm. AgBr.
III. 0.1680 grm. substance gave 0.3476 grm. AgBr.

| | Calculated for $C_4H_2Br_6O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 8.79 | 8.76 | | |
| H | 0.37 | 0.43 | | |
| Br | 87.90 | | 88.22 | 88.04 |

This substance will be more fully studied and the results presented to the Academy at a future time. The action of bromine upon the δ-monobrompyromucic acid under the conditions we have chosen may therefore be expressed by the following equations: —

$$C_5H_3BrO_3 + 2\ Br_2 + 3\ H_2O = C_4H_4O_4 + CO_2 + 5\ HBr.$$
$$C_5H_3BrO_3 + 3\ Br_2 + 3\ H_2O = C_4H_4Br_2O_4 + CO_2 + 5\ HBr.$$
$$C_5H_3BrO_3 + 3\ Br_2 = C_4H_2Br_6O + CO_2 + HBr.$$

*Action of Nitric Acid.*

On warming δ-monobrompyromucic acid with dilute nitric acid it is readily oxidized, carbonic dioxide is given off in abundance, and a small quantity of a yellowish oil distils over, which has not yet been further examined. For the complete oxidation of the acid we have found it best to take an equal weight of nitric acid (sp. gr. 1.42), diluted with four times its weight of water. The solution on cooling deposits crys-

tals of fumaric acid, and still more may be obtained by evaporation. The weight of fumaric acid thus obtained amounted to a little more than sixty per cent of that calculated from the equation,

$$C_5H_3BrO_3 + 2\ O + H_2O = C_4H_4O_4 + CO_2 + HBr.$$

The acid recrystallized from water and dried at 100° gave on analysis the following results: —

0.1728 grm. substance gave 0.2613 grm. $CO_2$ and 0.0575 grm. $H_2O$.

| | Calculated for $C_4H_4O_4$. | Found. |
|---|---|---|
| C | 41.37 | 41.24 |
| H | 3.45 | 3.70 |

Beside the fumaric acid could be isolated a small quantity of an acid readily soluble in cold water, whose melting-point suggested the possibility of its being maleic acid. Since at the high temperature which we had employed in oxidation it was to be expected that the maleic acid formed would be almost entirely converted into fumaric acid, we repeated the oxidation with stronger nitric acid (sp. gr. 1.42) and kept the temperature carefully between 30° and 35°. At this temperature the oxidation went on vigorously, and constant cooling was necessary. For complete oxidation three parts of strong nitric acid were found to be advantageous. After the oxidation was complete, the gaseous products of the reaction were removed by a current of air, the solution was then diluted, filtered from a slight flocculent precipitate thus formed, and neutralized with baric hydrate. In this way was precipitated a sparingly soluble crystalline barium salt, which, when recrystallized from hot water and dried by exposure to the air, proved to have the percentage composition of baric maleate.

I. 1.0940 grm. of the air-dried salt lost at 158° 0.0794 grm. $H_2O$.
II. 0.7644 grm. of the air-dried salt lost at 160° 0.0551 grm. $H_2O$.

| | Calculated for $BaC_4H_2O_4 . H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 6.69 | 7.26 | 7.21 |

I. 0.5036 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.4675 grm. $BaSO_4$.
II. 0.2776 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2579 grm. $BaSO_4$.

| | Calculated for $BaC_4H_2O_4$. | Found. I. | II. |
|---|---|---|---|
| Ba | 54.58 | 54.58 | 54.62 |

From the barium salt we made the acid by exact precipitation with sulphuric acid, and recrystallized it first from ether and afterwards from water. The acid thus prepared melted at 131–132°,* was very soluble in cold water, and by heating with hydrochloric acid in aqueous solution was converted into an acid having all the physical properties of fumaric acid. By the method just described we obtained about fifty per cent of the weight of baric maleate theoretically required; and since the method of separation was necessarily imperfect, we have not hesitated to assume that in the oxidation of δ-monobrompyromucic acid with nitric acid maleic acid is the product first formed, and that the fumaric acid obtained in the oxidation at higher temperature results only from the further alteration of this. While we have been unable to prove as yet the formation of maleic acid in the oxidation with bromine, even under the most favorable conditions, it seems to us that there can be little doubt that the reaction in this case is also essentially the same. The occurrence of isodibromsuccinic acid among the products of the action of bromine, while it does not prove this view to be correct, certainly is in its favor.

## β-Monobrompyromucic Acid.

From either of the dibrompyromucic acids subsequently described may be obtained by careful reduction a new monobrompyromucic acid isomeric with that already described. Since the dibrompyromucic acid melting at 167–168° is more conveniently prepared in large quantity, we have used this in order to obtain material for investigation. We have obtained the best results by dissolving two parts of the acid in four parts of concentrated ammonic hydrate diluted with fourteen parts of water, and adding one part of zinc dust. The reduction begins at once, the solution becomes hot, and in a few minutes the reaction is completed. When the ammoniacal solution no longer gives with calcic chloride an immediate precipitate of the sparingly soluble calcium salt of the dibrompyromucic acid, it is filtered and acidified with hydrochloric acid. If the reduction has not been carried too far, the solution soon solidifies with fine felted needles of the β-monobrompyromucic acid. For the purification of the acid we have found it best to convert it into the calcium salt, and to reject that portion of the

* The melting-point of maleic acid is usually given as 130°, but Kékulé has recently given the higher melting-point 132°.— Ann. Chem. u. Pharm., ccxxiii. 186.

salt which first separates from a dilute solution. The acid obtained by acidifying the concentrated solution we have then recrystallized from hot water. The acid dried over sulphuric acid gave on analysis the following results. The material used in Analysis IV. was made from the dibrompyromucic acid melting at 191–192°.

I. 0.5336 grm. substance gave 0.6117 grm. $CO_2$ and 0.0828 grm. $H_2O$.
II. 0.1996 grm. substance gave 0.1967 grm. AgBr.
III. 0.2064 grm. substance gave 0.2031 grm. AgBr.
IV. 0.2115 grm. substance gave 0.2089 grm. AgBr.

| | Calculated for $C_5H_3BrO_3$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| C | 31.42 | 31.26 | | | |
| H | 1.57 | 1.72 | | | |
| Br | 41.89 | | 41.97 | 41.88 | 42.05 |

β-Monobrompyromucic acid is readily soluble in alcohol or ether, quite soluble in chloroform or benzol, more sparingly soluble in ligroin or carbonic disulphide. It is very readily soluble in hot water, and as the solution cools it separates at high temperatures as an oil; at lower temperatures, in fine silky needles, which melt at 128–129°. On heating, it sublimes readily without decomposition. The solubility of the acid in water at ordinary temperatures we determined by neutralizing the solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

I. 21.1125 grm. of a solution saturated at 20° gave 0.1598 grm. $BaSO_4$.
II. 15.7586 grm. of a solution saturated at 20° gave 0.1198 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the acid: —

| I. | II. |
|---|---|
| 1.24 | 1.25 |

*Baric β-Monobrompyromucate*, $Ba(C_5H_2BrO_3)_2H_2O$. — By neutralizing an aqueous solution of the acid with baric carbonate, and concentrating the solution on the water bath, we obtained the barium salt in the form of irregular leafy scales, which were sparingly soluble in cold water, readily in hot. The air-dried salt lost nothing over sulphuric acid, and proved to contain one molecule of water.

I. 0.9389 grm. of air-dried salt lost at 120° 0.0334 grm. $H_2O$.
II. 1.9210 grm. air-dried salt lost at 130° 0.0676 grm. $H_2O$.

| | Calculated for $Ba(C_5H_2BrO_3)_2H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 3.36 | 3.56 | 3.52 |

I. 0.8920 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.4005 grm. $BaSO_4$.
II. 0.6245 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2816 grm. $BaSO_4$.

| | Calculated for $Ba(C_5H_2BrO_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ba | 26.50 | 26.39 | 26.51 |

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 6.1243 grm. of a solution saturated at 20° gave on precipitation with $H_2SO_4$ 0.0581 grm. $BaSO_4$.
II. 3.3922 grm. of a solution saturated at 20° gave on precipitation with $H_2SO_4$ 0.0317 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 2.11 | 2.07 |

*Calcic β-Monobrompyromucate*, $Ca(C_5H_2BrO_3)_2 . 3\ H_2O$.—The calcium salt we prepared by neutralizing an aqueous solution of the acid with calcic carbonate. It crystallizes in small clustered branching needles, which are sparingly soluble in cold water, more readily in hot. The salt is permanent in the air, but effloresces over sulphuric acid.

I. 1.1627 grm. of the air-dried salt lost at 120° 0.1314 grm. $H_2O$.
II. 1.8043 grm. of the air-dried salt lost at 120° 0.2047 grm. $H_2O$.

| | Calculated for $Ca(C_5H_2BrO_3)_2 . 3\ H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 11.40 | 11.30 | 11.34 |

I. 0.4784 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1534 grm. $CaSO_4$.
II. 0.5696 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1838 grm. $CaSO_4$.

| | Calculated for $Ca(C_5H_2BrO_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ca | 9.53 | 9.43 | 9.49 |

The solubility of the salt in cold water we determined by precipitating the saturated solution with ammonic oxalate, and converting the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

I. 11.3923 grm. of a solution saturated at 20° gave 0.0642 grm. $CaSO_4$.
II. 11.2016 grm. of a solution saturated at 20° gave 0.0625 grm. $CaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
| --- | --- |
| 1.74 | 1.72 |

*Argentic β-Monobrompyromucate*, $AgC_5H_2BrO_3$. — The silver salt is precipitated by the addition of argentic nitrate to an aqueous solution of the acid. For analysis, we prepared it from the sodium salt by precipitation, and purified it by recrystallization from hot water.

0.2503 grm. of the salt gave on precipitation with HBr 0.1586 grm. AgBr.

| | Calculated for $AgC_5H_2BrO_3$. | Found. |
| --- | --- | --- |
| Ag | 36.24 | 36.41 |

*Sodic β-Monobrompyromucate*, $NaC_5H_2BrO_3$.— The sodium salt prepared by neutralizing an aqueous solution of the acid with sodic carbonate crystallized in globular masses and proved to be anhydrous.

I. 0.4338 grm. of the salt gave on ignition with $H_2SO_4$ 0.1470 grm. $Na_2SO_4$.
II. 0.5577 grm. of the salt gave on ignition with $H_2SO_4$ 0.1849 grm. $Na_2SO_4$.

| | Calculated for $NaC_5H_2BrO_3$. | Found. I. | Found. II. |
| --- | --- | --- | --- |
| Na | 10.80 | 10.98 | 10.74 |

*Potassic β-Monobrompyromucate*, $KC_5H_2BrO_3$. — On neutralizing the acid in aqueous solution with potassic carbonate we obtained the potassium salt in the form of flat rectangular plates which proved to be anhydrous.

I. 0.3443 grm. of the salt gave on ignition with $H_2SO_4$ 0.1293 grm. $K_2SO_4$.

II. 0.4727 grm. of the salt gave on ignition with $H_2SO_4$ 0.1775 grm. $K_2SO_4$.

| | Calculated for $KC_5H_2BrO_3$. | Found. I. | II. |
|---|---|---|---|
| K | 17.07 | 16.86 | 16.86 |

*Ethyl β-Monobrompyromucate*, $(C_2H_5)C_5H_2BrO_3$. — The ethyl ether we have made by the action of ethyl iodide upon the silver salt, and also by heating a solution of the acid in absolute alcohol with concentrated sulphuric acid. It may conveniently be prepared by warming for several hours five parts of the acid with a mixture of five parts of absolute alcohol and three parts of concentrated sulphuric acid. A portion of the ether separates while the mixture is still hot, the rest may be precipitated after cooling by the addition of water. The product, well washed with water and a dilute solution of sodic carbonate, solidifies at low temperatures, and may be purified by repeated melting and pressing with filter-paper the crystals obtained by cooling. The ether crystallizes in transparent clustered prisms, and has a fragrant odor not unlike that of ethyl pyromucate. We found that it distilled without decomposition at 235–236° (mercury column completely in vapor) under a pressure of 768 mm., and that the greater portion boiled steadily at 235°. The thermometer in the solidifying distillate stood at 28°, while the melting-point, determined in the ordinary way in a capillary tube, we found to be 28–29°. The ether prepared from the silver salt by the action of ethyl iodide had the same melting-point, and was used in Analysis II.

I. 0.2194 grm. substance gave 0.1888 grm. AgBr.
II. 0.2120 grm. substance gave 0.1820 grm. AgBr.

| | Calculated for $(C_2H_5)C_5H_2BrO_3$. | Found. I. | II. |
|---|---|---|---|
| Br | 36.52 | 36.64 | 36.55 |

*β-Monobrompyromucamide*, $C_5H_2BrO_2NH_2$. — From the ethyl ether of β-monobrompyromucic acid can readily be made the corresponding amide by the action of concentrated aqueous ammonia, since the reaction progresses quite rapidly even at ordinary temperatures. The resulting product, when repeatedly crystallized from boiling water, formed fine silky needles which melted at 155–156°. It was readily soluble in alcohol, quite readily soluble in ether or boiling chloroform, more sparingly soluble in benzol, and almost insoluble in carbonic

disulphide or ligroin. It was readily soluble in hot water, but sparingly soluble in cold water.

0.6771 grm. substance gave 46.5 c.c. of moist nitrogen at 22.5° and under a pressure of 741 mm.

| | Calculated for $C_5H_2BrO_2NH_2$. | Found. |
|---|---|---|
| N | 7.37 | 7.74 |

$\beta$-monobrompyromucic acid appears to form no stable addition product with bromine. When exposed to the vapors of bromine for two days, we found that it had gained but 30 per cent of its weight, while a gain of 168 per cent was required for the formation of a tetrabromide. This slight gain in weight and the abundant evolution of hydrobromic acid pointed to the formation of a dibrompyromucic acid, for which a gain of 41 per cent was required. The product gave little evidence of decomposition when boiled with water, and was almost wholly soluble in a dilute solution of sodic carbonate. When recrystallized once from glacial acetic acid it melted at 165–166°, and possessed the characteristic properties of $\beta\delta$-dibrompyromucic acid. Bromine at ordinary temperatures had therefore replaced one atom of hydrogen by bromine.

### *Action of Bromine and Water.*

When $\beta$-monobrompyromucic acid is treated with bromine in aqueous solution it is rapidly oxidized, and products are formed which are apparently analogous to those formed from pyromucic acid under similar conditions. One or two molecules of bromine were readily taken up in the cold. In either case, the clear aqueous solution, when extracted with ether, yielded viscous oily products which showed no signs of crystallization after standing for days in vacuo over sulphuric acid. The extremely uninviting character of these substances made us unwilling to spend more time upon them at present, more especially since we found that mucobromic acid was formed when three molecules of bromine were employed. The reaction in this case required heat for its completion, and from the concentrated solution mucobromic acid (melting-point 120–121°) crystallized on cooling. Since it is probable that the aldehyde acid with one bromine atom corresponding to mucobromic acid is formed by the action of two molecules of bromine, we hope in the future to study the reaction further.

*Action of Nitric Acid.*

$\beta$-monobrompyromucic acid is readily oxidized by dilute nitric acid. In order to determine the product formed, we heated the acid with twice its weight of concentrated nitric acid (sp. gr. 1.42) diluted with five times its weight of water. After the oxidation was complete, we extracted the solution thoroughly with ether, and obtained, on evaporating the ether, a white crystalline acid which was readily soluble in water. After recrystallization from water it melted at 176–177°, and gave a percentage of bromine, which showed it to be monobromfumaric acid (isobrommaleic acid).

0.2300 grm. substance gave 0.2218 grm. AgBr.

| | Calculated for $C_4H_3BrO_4$. | Found. |
|---|---|---|
| Br | 41.03 | 41.04 |

By oxidation with nitric acid monobromfumaric acid had therefore been formed according to the equation,

$$C_5H_3BrO_3 + 3\ O = C_4H_3BrO_4 + CO_2.$$

## Ethyl Pyromucate with one Molecule of Bromine.

We have made six fruitless attempts to prepare a monobrompyromucic acid melting at 156–157°, according to the method described by Schiff and Tassinari,* by the addition of one molecule of bromine to ethyl pyromucate, and the decomposition of the product thus obtained by an alcoholic solution of potassic hydrate. Aside from the $\delta$-monobrompyromucic acid, which could readily be isolated, we have been able to find only the two isomeric dibrompyromucic acids hereafter described which result from the decomposition of the tetrabromide of the ethyl ether. In separating these two acids we followed the method which we had already found most efficacious, namely, the fractional crystallization of the calcium salts, but in other respects we adhered strictly to the directions given by Schiff and Tassinari. The acid obtained from the less soluble calcium salt melted at 166–167°, and crystallized from water in the twinned forms characteristic of the $\beta\delta$-dibrompyromucic acid.

0.1444 grm. substance gave 0.2020 grm. AgBr.

| | Calculated for $C_5H_2Br_2O_3$. | Found. |
|---|---|---|
| Br | 59.26 | 59.53 |

* Gazzetta Chimica, viii. 298.

From the more soluble calcium salt we obtained the $\beta\gamma$-dibrompyromucic acid melting at 190–192°, which gave on analysis the proper percentage of bromine.

0.1955 grm. substance gave 0.2723 grm. AgBr.

| | Calculated for $C_5H_2Br_2O_3$. | Found. |
|---|---|---|
| Br | 59.26 | 59.29 |

Furthermore, it was not difficult to isolate in considerable quantity an acid containing but a trace of bromine, which melted at 129–130°, and which possessed in other respects the character of pyromucic acid. Our observations agree closely with those described by Canzoneri and Oliveri in the paper already mentioned,* with the single exception that they appear to have overlooked entirely the formation of the second dibrompyromucic acid melting at 167–168°. Since the two dibrompyromucic acids and unaltered pyromucic acid were formed from a product containing equal molecules of ethyl pyromucate and bromine, we were led to the conclusion that no dibromide had been formed under the conditions chosen, and that the supposed dibromide was in fact only a mixture of unaltered pyromucic ether with its tetrabromide. Since at ordinary temperatures quantities of hydrobromic acid were evolved on mixing the pyromucic ether with bromine,† (a fact not mentioned by Schiff and Tassinari or by Canzoneri and Oliveri,) it was evident that the monobrompyromucic acid which appeared among the products could readily have been formed by direct substitution. On submitting the mixture of equal molecules of pyromucic ether and bromine to fractional distillation in vacuo, it was easy to isolate among the more volatile products the ethyl ether of $\delta$-monobrompyromucic acid and ethyl pyromucate, melting at 34–35°. The ethyl monobrompyromucate still contained ethyl pyromucate, since the percentage of bromine which we found was much too low.

0.1890 grm. substance gave 0.1487 grm. AgBr.

| | Calculated for $(C_2H_5)C_5H_2BrO_3$. | Found. |
|---|---|---|
| Br | 36.54 | 33.49 |

The acid obtained from the ether, when recrystallized from water, melted at 182–183°.

* Gazzetta Chimica, xiv. 173.

† The evolution of hydrobromic acid was invariably observed, although we varied in many ways the conditions under which the reaction took place. In addition to the glacial acetic acid recommended by Schiff and Tassinari as a solvent, we tried carbonic disulphide and chloroform with the same results.

## Action of Alcoholic Sodic Hydrate upon Pyromucic Tetrabromide.

By acting upon pyromucic tetrabromide with an alcoholic solution of potassic hydrate, Toennies obtained a dibrompyromucic acid melting at 186°. In the preliminary paper already referred to,* he gives no description of the conditions under which the decomposition was effected, and, as far as we are aware, he has never published any more extended account of his work.

The pyromucic tetrabromide we prepared according to his directions by exposing pyromucic acid to the vapors of bromine. The bromine was quite rapidly absorbed, and the acid was converted into a voluminous porous mass from which the excess of bromine could readily be expelled by a short exposure to the air. The formation of this addition product, however, was not the only reaction which took place, since hydrobromic acid was invariably evolved in no insignificant quantities, and the product therefore contained also δ-monobrompyromucic acid and its tetrabromide. For the purification of the pyromucic tetrabromide we have found glacial acetic acid (99.5 per cent) more advantageous than the mixture of ligroin and ether recommended by Toennies.

Since the purification of large quantities of the tetrabromide was at best a matter of difficulty, we have used in our work the crude product, more especially since the isolation of the products formed from it presented no greater difficulties. Instead of using an alcoholic solution of potassic hydrate for its decomposition, we have taken sodic hydrate, since the sodium salts of the acids formed seemed to be somewhat less soluble in alcohol than the potassium salts. We have found that the best results may be obtained by using a decided excess of a concentrated solution of the alkaline hydrate, taking care that the temperature does not rise above 25°. The greater part of the sodium salts formed separates at once, and may be filtered off upon the pump. The sodium salt dissolved in water and acidified with hydrochloric acid yields an acid, usually more or less colored, which is readily soluble in cold water, more readily in hot, and whose melting-point is quite constant (136–138°). This consists essentially of a mixture of two isomeric dibrompyromucic acids, although it frequently contains small quantities of δ-monobrompyromucic and tribrompyromucic acids. The aqueous solution filtered from these acids contains also oxalic acid.

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* Berichte der deutschen chem. Gesellsch., xi. 1086.

Although we have not found it possible to separate these acids directly by fractional crystallization, they may be separated by means of their calcium salts. While we have found it easy to prepare in this way small quantities of the pure acids, the complete separation of large quantities of the acids involves a very considerable amount of time and labor. We have found it most convenient to dissolve the mixed acids in ammonic hydrate, and to add calcic chloride to the dilute solution (1 : 30). A very sparingly soluble crystalline calcium salt is thus thrown down, which contains chiefly one of the two dibrompyromucic acids, while the calcium salts of the other acids remain in solution. The sparingly soluble calcium salt may be purified by recrystallization from boiling water, or the acid may be set free, the calcium salt reprecipitated, and the operation repeated until the melting-point of the acid is found to be 164–166°. The solution containing the more soluble calcium salts is acidified, and the acids thus obtained are separated by recrystallization from boiling water. The tribrompyromucic acid is almost insoluble in water, while the δ-monobrompyromucic acid, though but slightly more soluble in cold water than the dibrompyromucic acid, is present in such small quantity that its removal is a matter of little difficulty. When the melting-point of the dibrompyromucic acid has been raised to 184° by recrystallization from water, its further purification is effected by washing or recrystallizing from benzol. The acid whose calcium salt is more sparingly soluble in water, and which, as we shall afterward show, is the βδ-dibrompyromucic acid, melts at 167–168°, while the isomeric βγ-dibrompyromucic acid, whose calcium salt is more readily soluble, melts at 191–192°. Although we have made many attempts to control at will the quantities of the two dibrompyromucic acids formed, we have as yet met with no success. The yield of the mixed acids was far from satisfactory, and amounted to but from thirty-four to thirty-eight per cent of that theoretically required. The difficulties in the way of complete separation of the two acids make it impossible for us to give the precise ratio between the amounts of the two isomers found. While we have usually obtained nearly twice as much of the low-melting acid as of the high, we are inclined to think that the original mixture contained them in nearly equal quantities.

The alcoholic filtrate from the sodium salts contained, beside small quantities of these salts in solution, considerable quantities of sodic δ-monobrompyromucate. When diluted with water, it became turbid, with the separation of a small quantity of a colorless oil. In order to determine its nature, we distilled the filtrate with steam and precipi-

tated the alcoholic distillate by the further addition of water. The oil which was thus thrown down was dried with calcic chloride and distilled under diminished pressure. The wide range in boiling-point (60–130° at 17 mm.) which we then observed showed its nature to be tolerably complex. After repeated distillations, we were able to isolate one fraction (A) boiling between 59° and 69° under 17 mm. pressure, and a somewhat larger fraction boiling at 94–99° under a pressure of 17 mm. This second fraction partially solidified on standing, and the crystals (B) were separated from the oily mother-liquor (C) by filtration. With a second larger quantity of the alcoholic filtrate subsequently obtained we adopted a somewhat different method. We precipitated the excess of sodic hydrate by carbonic dioxide, distilled the alcoholic filtrate, and precipitated the distillate with water. After several distillations in vacuo, we obtained one fraction (D) boiling at 57–62° under a pressure of 20 mm., a second (E) boiling at 61–68° under a pressure of 19 mm., and a third boiling at 98–102° under a pressure of 19 mm., which as before partially solidified on standing, and the crystals (F) were separated by filtration from the mother-liquor (G). The fractions boiling between 68° and 98° were insignificant in quantity.

The lower boiling fractions proved, on analysis, to contain a percentage of bromine, agreeing closely with that required by the formula $C_4H_2Br_2O$.

I. 0.2444 grm. of substance (A) gave 0.4060 grm. AgBr.
II. 0.2503 grm. of substance (A) gave 0.4160 grm. AgBr.
III. 0.3593 grm. of substance (D) gave 0.5959 grm. AgBr.
IV. 0.2559 grm. of substance (E) gave 0.4284 grm. AgBr.
V. 0.3416 grm. of substance (E) gave 0.5715 grm. AgBr.

| | Calculated for $C_4H_2Br_2O$. | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| Br | 70.79 | 70.69 | 70.74 | 70.58 | 71.25 | 71.19 |

The great variation in boiling-point with this slight variation in percentage composition renders it probable that the oil contained two isomeric dibromfurfurans. The fraction boiling at 61–68°, after standing for a few days, was unfortunately largely converted into an amorphous black solid; the lower fraction remained unaltered. When the lower fraction was treated with bromine, hydrobromic acid was evolved even at ordinary temperatures, so that no corresponding addition product could be prepared, and we have hitherto been unable to obtain

by oxidation any products which would enable us to draw any conclusion as to its constitution.

The solid which separated from the higher fractions, on cooling when recrystallized from alcohol, formed broad flattened needles which melted at 77°. It was readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in carbonic disulphide or ligroin. The percentage of bromine which the substance contained agreed precisely with that required by the formula $C_4H_8BrO_2$. While the combustion of the substance gave a percentage of carbon materially greater than that which this formula requires, it seemed to us to leave no doubt of the composition of the substance. We were therefore unwilling to sacrifice the small amount of the substance which we had left in order to make a second combustion.

I. 0.5251 grm. of substance (F) gave 0.5742 grm. $CO_2$ and 0.0949 grm. $H_2O$.
II. 0.1523 grm. of substance (B) gave 0.1758 grm. AgBr.
III. 0.2186 grm. of substance (F) gave 0.2527 grm. AgBr.

| | Calculated for $C_4H_3BrO_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 29.44 | 29.82 | | |
| H | 1.84 | 2.01 | | |
| Br | 49.09 | | 49.14 | 49.19 |

The small amount of this substance at our disposal — we obtained but three grammes of the crude product from 2.6 kilogrammes of pyromucic tetrabromide — has made it impossible for us to submit it to any very extended investigation. In aqueous solution it reduces silver oxide, and at the same time argentic bromide is formed. We were unable, however, to isolate any definite products of the oxidation. With nitric acid, apparently nothing but oxalic acid was formed. It was unaffected by dry bromine, but when treated with bromine and water it was converted into an amorphous substance insoluble or sparingly soluble in all common solvents. It was readily decomposed by aqueous alkalies. The solution had a bright yellow color, and contained potassic bromide, but we have been unable to determine the products resulting from the reaction.

This ready decomposition in alkaline solution makes it probable that it was formed during the process of distillation, although it is perhaps possible that the small quantity which we were able to obtain was only that portion which chanced to escape decomposition in the

original alkaline solution. It will be noticed that this substance is isomeric with a product obtained by Limpricht by the action of bromine upon pyromucic acid under conditions which he was unable to fix precisely. The higher melting-point, 84°, and the fact that it was unaffected by an alcoholic solution of potassic hydrate at 180°, establish with sufficient precision their essential difference.

The higher boiling fractions from which this crystalline substance had been separated as completely as possible gave, on analysis, a percentage of bromine, which showed that they consisted mainly of a tribromfurfuran. The difficulty of removing completely, by distillation or by freezing, the solid constituent, sufficiently explains the low percentages of bromine we have obtained.

I. 0.2312 grm. of substance (C) gave 0.4130 grm. AgBr.
II. 0.3253 grm. of substance (C) gave 0.5855 grm. AgBr.
III. 0.2897 grm. of substance (G) gave 0.5246 grm. AgBr.
IV. 0.2291 grm. of substance (G) gave 0.4130 grm. AgBr.

| | Calculated for $C_4HBr_3O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Br | 78.68 | 76.03 | 76.61 | 77.05 | 76.74 |

This tribromfurfuran, when treated with bromine, gave off at ordinary temperatures clouds of hydrobromic acid, so that the corresponding addition product could not be prepared. We have also been unable as yet to obtain any definite oxidation products containing four carbon atoms.

The formation of dibromfurfuran from pyromucic tetrabromide evidently takes place according to the equation,

$$C_5H_4Br_4O_3 = C_4H_2Br_2O + CO_2 + 2\ HBr.$$

The tribromfurfuran must, of necessity, be formed from the monobrompyromucic tetrabromide which the crude pyromucic tetrabromide contains, —

$$C_5H_3Br_5O_3 = C_4HBr_3O + CO_2 + 2\ HBr.$$

### $\beta\delta$-Dibrompyromucic Acid.

This acid is formed, as has already been explained, together with the isomeric $\beta\gamma$-dibrompyromucic acid, by the action of an alcoholic solution of sodic hydrate upon pyromucic tetrabromide. It may, how-

ever, be more conveniently, if not more economically, prepared by the direct action of bromine upon pyromucic acid. The reaction is apparently quite complex, a large excess of bromine is required, and the product is small compared with that theoretically required. Pyromucic acid is treated with about three molecules of bromine, and heated on the water bath with reverse cooler, until the evolution of hydrobromic acid is over. There remains, then, in the flask a red viscous oil which contains $\beta\delta$-dibrompyromucyl bromide with a small amount of $\delta$-monobrompyromucyl bromide, dibrommaleic acid or its anhydride, and other products not yet more exactly determined. This oil is washed with cold water to remove the more soluble products, and is then boiled with water until the acid bromides are converted into the acids. The separation of the dibrompyromucic from the monobrompyromucic acid with which it is mixed may be most conveniently effected by precipitating its barium salt from an ammoniacal solution by the addition of baric chloride, and repeating the operation until a product melting at 165-166° is obtained. By subsequent recrystallization from hot water and from benzol the melting-point may then be raised to 167–168°.

The acid thus purified gave, on analysis, the following results: —

I. 0.5370 grm. substance gave 0.4379 grm. $CO_2$ and 0.0390 grm. $H_2O$.
II. 0.2251 grm. substance gave 0.3125 grm. AgBr.
III. 0.1665 grm. substance gave 0.2323 grm. AgBr.

| | Calculated for $C_5H_2Br_2O_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 22.22 | 22.24 | | |
| H | 0.74 | 0.81 | | |
| Br | 59.26 | | 59.09 | 59.39 |

The $\beta\delta$-dibrompyromucic acid is readily soluble in alcohol or ether, freely soluble in boiling chloroform, quite readily soluble in benzol, but sparingly soluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, quite readily soluble in boiling water, and crystallizes on cooling in small oblique prisms, which, however, usually appear in characteristic twinned forms.

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the saturated solution, and determining by precipitation with sulphuric acid the amount of barium dissolved.

I. 38.3346 grm. of a solution saturated at 20° gave 0.0462 grm. $BaSO_4$.
II. 38.3935 grm. of a solution saturated at 20° gave 0.0464 grm. $BaSO_4$.

According to these determinations the aqueous solution of the acid saturated at 20° contained the following percentages: —

| I. | II. |
|---|---|
| 0.28 | 0.28 |

*Baric βδ-Dibrompyromucate*, $Ba(C_5HBr_2O_3)_2 . 4 H_2O$. — The barium salt we prepared by neutralizing a boiling aqueous solution of the acid with baric carbonate. After recrystallization from boiling water, it formed fine branching needles. The air-dried salt contained four molecules of water, three of which it lost over sulphuric acid.

I. 1.4800 grm. of air-dried salt lost 0.1117 grm. $H_2O$ over sulphuric acid, and in addition 0.0324 grm. $H_2O$ at 110°.
II. 2.1113 grm. of the air-dried salt lost at 110° 0.2030 grm. $H_2O$.

| | Calculated for $Ba(C_5HBr_2O_3)_2 . 4 H_2O$. | Found. I. | II. |
|---|---|---|---|
| 3 $H_2O$ | 7.23 | 7.54 | |
| 4 $H_2O$ | 9.64 | 9.74 | 9.60 |

I. 0.4109 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1415 grm. $BaSO_4$.
II. 0.7780 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2666 grm. $BaSO_4$.

| | Calculated for $Ba(C_5HBr_2O_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ba | 20.30 | 20.24 | 20.14 |

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 38.7621 grm. of a solution saturated at 16° gave 0.0132 grm. $BaSO_4$.
II. 36.2526 grm. of a solution saturated at 16° gave 0.0129 grm. $BaSO_4$.

The aqueous solution saturated at 16° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 0.10 | 0.10 |

*Calcic βδ-Dibrompyromucate*, $Ca(C_5HBr_2O_3)_2 . 3 H_2O$. — On neutralizing a boiling aqueous solution of the acid with calcic carbonate, we obtained the calcium salt in small clustered prisms, which we purified by recrystallization from boiling water. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid.

I. 1.1374 grm. of air-dried salt lost over sulphuric acid 0.0275 grm. $H_2O$, and in addition 0.0706 grm. $H_2O$ at 110°.

II. 1.4733 grm. of the air-dried salt lost at 112° 0.0984 grm. $H_2O$.

| | Calculated for $Ca(C_5HBr_2O_3)_2 . 3 H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| $H_2O$ | 2.85 | 2.42 | |
| $3 H_2O$ | 8.56 | 8.63 | 8.36 |

I. 0.4709 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1107 grm. $CaSO_4$.

II. 0.6026 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1387 grm. $CaSO_4$.

| | Calculated for $Ca(C_5HBr_2O_3)_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Ca | 6.92 | 6.91 | 6.77 |

The solubility of the salt in cold water we determined by evaporation and ignition with sulphuric acid.

I. 39.5194 grm. of a solution saturated at 17° gave 0.0288 grm. $CaSO_4$.

II. 50.3735 grm. of a solution saturated at 17° gave 0.0344 grm. $CaSO_4$.

The aqueous solution saturated at 17° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 0.31 | 0.29 |

*Argentic βδ-Dibrompyromucate*, $AgC_5HBr_2O_3$. — From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of fine clustered needles, which may be recrystallized from hot water without essential decomposition. For analysis we prepared it by precipitating a solution of argentic nitrate with a solution of the acid neutralized by ammonic hydrate.

0.3275 grm. of the salt dried over sulphuric acid gave 0.1646 grm. AgBr.

| | Calculated for $AgC_5HBr_2O_3$. | Found. |
|---|---|---|
| Ag | 28.65 | 28.87 |

*Sodic βδ-Dibrompyromucate*, $NaC_5HBr_2O_3 . 2 H_2O$. — The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate, and subsequent recrystallization from water. It formed short needles, which were not very soluble in cold water, and which, when air-dried, contained two molecules of water.

I. 1.0207 grm. of the air-dried salt lost at 122° 0.1095 grm. $H_2O$.
II. 1.1177 grm. of the air-dried salt lost at 122° 0.1201 grm. $H_2O$.

| | Calculated for $NaC_5HBr_2O_3 . 2 H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 10.97 | 10.73 | 10.75 |

I. 0.5364 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1284 grm. $Na_2SO_4$.
II. 0.5492 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1314 grm. $Na_2SO_4$.

| | Calculated for $NaC_5HBr_2O_3$. | Found. I. | II. |
|---|---|---|---|
| Na | 7.88 | 7.76 | 7.75 |

*Potassic βδ-Dibrompyromucate*, $KC_5HBr_2O_3$. — The potassium salt prepared by dissolving the acid in a dilute solution of potassic carbonate, and recrystallizing the product thus obtained from water, crystallized in long concentrically grouped needles, which proved to be anhydrous.

I. 0.5986 grm. of the salt gave on ignition with $H_2SO_4$ 0.1691 grm. $K_2SO_4$.
II. 0.6018 grm. of the salt gave on ignition with $H_2SO_4$ 0.1680 grm. $K_2SO_4$.

| | Calculated for $KC_5HBr_2O_3$. | Found. I. | II. |
|---|---|---|---|
| K | 12.69 | 12.69 | 12.53 |

*Ethyl βδ-Dibrompyromucate*, $(C_2H_5)C_5HBr_2O_3$. — The ethyl ether we have made by the action of ethyl iodide upon the silver salt of the acid, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. By the latter method we have obtained a good yield by dissolving five parts of the acid in an equal weight of absolute alcohol, adding three parts of concentrated sulphuric acid, and warming for several hours at 100°. The product precipitated by the addition of water we washed with a dilute solution of sodic carbonate and purified by recrystallization from alcohol. It crystallized in small,

flat, clustered prisms, which melted at 57–58°, and boiled with decided decomposition at 271–272° (mercury column completely in vapor), under a pressure of 765 mm. The ether has a pleasant, fragrant odor, not unlike that of ethyl pyromucate. It is readily soluble in ether, chloroform, benzol, or ligroin, somewhat less soluble in carbonic disulphide. It is readily soluble in hot alcohol, much more sparingly soluble in cold. The ether used in Analysis II. was made from the silver salt.

I. 0.1524 grm. substance gave 0.1927 grm. AgBr.
II. 0.2024 grm. substance gave 0.2556 grm. AgBr.

| | Calculated for $(C_2H_5)C_5HBr_2O_3$. | Found. I. | II. |
|---|---|---|---|
| Br | 53.69 | 53.83 | 53.74 |

*βδ-Dibrompyromucyl Bromide*, $C_5HBr_3O_2$. — It has already been said that βδ-dibrompyromucyl bromide is formed by the action of dry bromine upon pyromucic acid. In order to isolate it, we submitted the viscous oil which was thus formed to fractional distillation in vacuo. After repeated distillations a fraction was isolated, boiling at 149–155° under a pressure of 24 mm., most of which passed over between 153° and 155°. This fraction, on standing over sulphuric acid, gradually solidified, and the solid thus obtained could readily be purified by recrystallization from ligroin. On heating with water it formed βδ-dibrompyromucic acid; with alcohol, it gave the ether melting at 56–57°; and on analysis it gave the percentage of bromine required by the formula $C_5HBr_3O_2$. Analysis III. was made with material prepared from the crude product by crystallization alone without previous distillation.

I. 0.2214 grm. substance gave 0.3752 grm. AgBr.
II. 0.1876 grm. substance gave 0.3180 grm. AgBr.
III. 0.2152 grm. substance gave 0.3640 grm. AgBr.

| | Calculated for $C_5HBr_3O_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Br | 72.07 | 72.11 | 72.14 | 71.99 |

The βδ-dibrompyromucyl bromide crystallizes in small compact prisms which melt at 45–46°. It is readily soluble in alcohol, ether, chloroform, or benzol, somewhat less soluble in ligroin. It is slowly attacked by cold water, more readily by hot.

From the lower fractions there separated, on standing, prismatic crystals, which, from their behavior and from their melting-point

(114–115°), were shown to be dibrommaleic anhydride. In confirmation we prepared from the aqueous solution obtained by washing the crude product with cold water considerable quantities of baric dibrommaleate, which was identified by analysis.

0.5423 grm. of the air-dried salt gave on ignition with $H_2SO_4$ 0.2853 grm. $BaSO_4$.

| | Calculated for $BaC_4Br_2O_4 . 2 H_2O$. | Found. |
|---|---|---|
| Ba | 30.78 | 30.93 |

Since the most volatile portions of the oil gave with water $\delta$-monobrompyromucic acid, it contained doubtless the corresponding monobrompyromucyl bromide. The quantity, however, appeared to be so small that we made no attempt to isolate it.

*$\beta\delta$-Dibrompyromucamide,* $C_5HBr_2O_2NH_2$. — Concentrated aqueous ammonia acts but slowly upon the ethyl ether of $\beta\delta$-dibrompyromucic acid, and even after long standing the decomposition is imperfect. The amide may readily be made from the bromide just described by the action of aqueous ammonia, and may be purified by recrystallization from hot water. Thus prepared, it forms long silky needles which melt at 175–176°. It is readily soluble in alcohol, quite readily soluble in ether, chloroform, or hot benzol, and almost insoluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, but freely soluble in hot water.

0.9102 grm. substance gave 44.5 c.c. moist nitrogen at 14.5° and under a pressure of 722 mm.

| | Calculated for $C_5HBr_2O_2NH_2$. | Found. |
|---|---|---|
| N | 5.20 | 5.31 |

## *Action of Bromine and Water.*

We found that the $\beta\delta$-dibrompyromucic acid was rather slowly attacked by bromine in aqueous solution, and the reaction appeared to be essentially the same whether the bromine was added rapidly or slowly. We therefore suspended the acid in water, and added at once rather more than two molecules of bromine, taking care to prevent any decided rise of temperature. Carbonic dioxide was slowly evolved, and the red oil which was at first formed gradually solidified. The product was then pressed with filter-paper, and recrystallized from boiling ligroin. Treatment with bone-black was usually necessary in order to obtain a colorless product. The substance thus

prepared was very readily soluble in alcohol, ether, chloroform, carbonic disulphide, or benzol, more sparingly soluble in ligroin, from which it crystallized in long lustrous prisms which melted at 55–56°. By the slow evaporation of the solution in ligroin quite large and well-developed individuals could be obtained. The substance dried over sulphuric acid gave on analysis the following results: —

I. 0.9663 grm. substance gave 0.5285 grm. $CO_2$ and 0.0300 grm. $H_2O$.
II. 0.2053 grm. substance gave 0.3594 grm. AgBr.
III. 0.2344 grm. substance gave 0.4109 grm. AgBr.

| | Calculated for $C_4HBr_3O_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 14.95 | 14.91 | | |
| H | 0.31 | 0.35 | | |
| Br | 74.76 | | 74.50 | 74.61 |

When boiled with water this substance was gradually decomposed, and the aqueous solution then appeared to contain a mixture of dibromsuccinic, monobromfumaric, and monobrommaleic acid, as far as could be determined from the melting-points and other physical properties of the products obtained by evaporation and recrystallization. Since we thought it not improbable that the dibromsuccinic and monobromfumaric acids had been formed from the monobrommaleic acid by the action of the hydrobromic acid formed in the reaction, we decomposed the substance by heating it with a dilute solution of potassic hydrate, added hydrochloric acid in quantity just sufficient to set the organic acid free, extracted with ether, and recrystallized from water the residue left upon evaporation of the ether. In this way we obtained a homogeneous product which melted at 126–127°, and which gave on analysis the percentage of bromine required by monobrommaleic acid.

0.2099 grm. substance gave 0.2013 grm. AgBr.

| | Calculated for $C_4H_3BrO_4$. | Found. |
|---|---|---|
| Br | 41.03 | 40.82 |

The chief product of the action of aqueous bromine upon $\beta\delta$-dibrompyromucic acid was therefore monobrommaleyl bromide formed according to the equation,

$$C_5H_2Br_2O_3 + 2\ Br_2 + H_2O = C_4HBr_3O_2 + CO_2 + 3\ HBr.$$

We have obtained usually about seventy per cent of the theoretical yield of monobrommaleyl bromide, and have been able to isolate no other products of the reaction except such as would naturally result from its decomposition with water.

*Action of Nitric Acid.*

The $\beta\delta$-dibrompyromucic acid is readily oxidized, with evolution of carbonic dioxide, by boiling even with dilute nitric acid. We have found two parts of strong nitric acid (sp. gr. 1.42), diluted with ten parts of water, sufficient for the complete oxidation of one part of the acid. After the reaction was ended, we extracted the solution with ether and crystallized from water the product obtained by the evaporation of the ether. This product appeared to contain nothing but an acid melting at 174–175°, which on analysis gave the percentage of bromine required by monobromfumaric acid.

0.2254 grm. substance gave 0.2186 grm. AgBr.

| | Calculated for $C_4H_3BrO_4$. | Found. |
|---|---|---|
| Br | 41.03 | 41.28 |

Since we have already shown that the product formed by the action of aqueous bromine is a derivative of monobrommaleic acid, we have not hesitated to assume that the first product of the oxidation with nitric acid also is monobrommaleic acid, and that this is converted into monobromfumaric acid by the continued boiling with nitric acid. The reaction may be written,

$$C_5H_2Br_2O_3 + O + H_2O = C_4H_3BrO_4 + CO_2 + HBr.$$

$\beta\gamma$-Dibrompyromucic Acid.

The formation of $\beta\gamma$-dibrompyromucic acid from the pyromucic tetrabromide has already been described, and we have not been able to find any other method for its preparation. For analysis, the acid was recrystallized several times from water, and finally from benzol.

I. 0.6274 grm. substance gave 0.5065 grm. $CO_2$ and 0.0445 grm. $H_2O$.
II. 0.2165 grm. substance gave 0.3019 grm. AgBr.
III. 0.2225 grm. substance gave 0.3106 grm. AgBr.

| | Calculated for $C_5H_2Br_2O_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 22.22 | 22.02 | | |
| H | 0.74 | 0.79 | | |
| Br | 59.26 | | 59.33 | 59.40 |

The $\beta\gamma$-dibrompyromucic acid crystallizes from benzol in short clustered prisms, from water in voluminous feather-like forms. It is readily soluble in ether or alcohol, quite readily soluble in boiling benzol or chloroform, and but sparingly soluble in carbonic disulphide or ligroin. It is rather sparingly soluble even in hot water, and still less soluble in cold water. The solubility of the acid in water at ordinary temperatures we determined by boiling the saturated solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

I. 53.3668 grm. of a solution saturated at 20° gave 0.0481 grm. $BaSO_4$.
II. 50.6792 grm. of a solution saturated at 20° gave 0.0477 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the acid: —

| I. | II. |
|---|---|
| 0.21 | 0.22 |

*Baric $\beta\gamma$-Dibrompyromucate*, $Ba(C_5HBr_2O_3)_2 . 3 H_2O$. — The barium salt we made by precipitating with baric chloride a dilute ammoniacal solution of the acid, and recrystallizing from boiling water the salt thus precipitated. It formed irregular radiating flattened needles which effloresced over sulphuric acid, but which contained three molecules of water when dried by exposure to the air.

I. 1.6173 grm. of the air-dried salt lost at 150° 0.1226 grm. $H_2O$.
II. 1.1994 grm. of the air-dried salt lost at 130° 0.0847 grm. $H_2O$.

| | Calculated for $Ba(C_5HBr_2O_3)_2 . 3 H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 7.41 | 7.58 | 7.06 |

I. 1.4947 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.5197 grm. $BaSO_4$.
II. 0.4555 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1544 grm. $BaSO_4$.

| | Calculated for $Ba(C_5HBr_2O_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ba | 20.30 | 20.44 | 19.93 |

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 41.9064 grm. of a solution saturated at 20° gave 0.0521 grm. $BaSO_4$.
II. 37.7244 grm. of a solution saturated at 20° gave 0.0449 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 0.36 | 0.34 |

*Calcic βγ-Dibrompyromucate*, $Ca(C_5HBr_2O_3)_2 . 5 H_2O$. — The calcium salt we made by boiling the acid with water and adding calcic carbonate. The salt recrystallized from boiling water formed concentrically grouped needles, which effloresced slowly in the air, rapidly over sulphuric acid.

I. 1.7504 grm. of the salt lost at 120° 0.2330 grm. $H_2O$.
II. 2.4934 grm. of the salt lost at 120° 0.3300 grm. $H_2O$.

| | Calculated for $Ca(C_5HBr_2O_3)_2 . 5 H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 13.47 | 13.31 | 13.23 |

I. 0.5620 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1301 grm. $CaSO_4$.
II. 0.8701 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2011 grm. $CaSO_4$.

| | Calculated for $Ca(C_5HBr_2O_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ca | 6.92 | 6.81 | 6.80 |

The solubility of the salt in water at ordinary temperatures we determined by precipitating a saturated solution with ammonic oxalate, and igniting the calcic oxalate thus obtained with sulphuric acid.

I. 20.5686 grm. of a solution saturated at 20° gave 0.0561 grm. $CaSO_4$.
II. 19.7985 grm. of a solution saturated at 20° gave 0.0538 grm. $CaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 1.16 | 1.15 |

*Argentic βγ-Dibrompyromucate,* $AgC_5HBr_2O_3$. — From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of minute clustered needles, which dissolve without essential decomposition on heating the solution. For analysis we prepared it by precipitating with argentic nitrate a neutral solution of the acid in dilute ammonic hydrate.

0.2584 grm. of the salt gave on precipitation with HBr 0.1297 grm. AgBr.

| | Calculated for $AgC_5HBr_2O_3$. | Found. |
|---|---|---|
| Ag | 28.65 | 28.83 |

*Sodic βγ-Dibrompyromucate,* $NaC_5HBr_2O_3 . 2\ H_2O$. — The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate and recrystallizing from water the salt thus obtained. It formed fine silky needles, which were not very soluble in cold water. The air-dried salt contained two molecules of water.

I. 2.0032 grm. of the air-dried salt lost at 119° 0.2192 grm. $H_2O$.
II. 1.7440 grm. of the air-dried salt lost at 119° 0.1925 grm. $H_2O$.

| | Calculated for $NaC_5HBr_2O_3 . 2\ H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| $H_2O$ | 10.97 | 10.94 | 11.04 |

I. 0.6162 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1502 grm. $Na_2SO_4$.
II. 0.6275 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1506 grm. $Na_2SO_4$.

| | Calculated for $NaC_5HBr_2O_3$. | Found. I. | Found. II. |
|---|---|---|---|
| Na | 7.88 | 7.90 | 7.78 |

*Potassic βγ-Dibrompyromucate,* $KC_5HBr_2O_3$. — The potassium salt made by neutralizing the acid with potassic carbonate crystallized in flat clustered prisms, which were not very soluble in cold water and were anhydrous.

I. 0.5082 grm. of the salt gave on ignition with $H_2SO_4$ 0.1390 grm. $K_2SO_4$.

II. 0.9303 grm. of the salt gave on ignition with $H_2SO_4$ 0.2603 grm. $K_2SO_4$.

| | Calculated for $KC_5HBr_2O_3$. | Found. I. | II. |
|---|---|---|---|
| K | 12.69 | 12.57 | 12.56 |

*Ethyl βγ-Dibrompyromucate,* $(C_2H_5)C_5HBr_2O_3$. — The ethyl ether we have prepared by the action of ethyl iodide upon the silver salt of the acid, and also by heating the acid in alcoholic solution with concentrated sulphuric acid. For its preparation by the latter method we used the same proportions which we had already found advantageous in the case of the βδ-dibrompyromucic acid; namely, five parts of the acid, five of absolute alcohol, and three of concentrated sulphuric acid. The reaction was completed in a few hours at 100°, and the ether was precipitated with water, washed with a dilute solution of sodic carbonate, and recrystallized from alcohol. Thus prepared, it formed fine silky needles which melted at 67–68°. Its odor recalled at the same time ethyl pyromucate and anise. It is readily soluble in ether, chloroform, benzol, carbonic disulphide, ligroin, or hot alcohol, sparingly soluble in cold alcohol. The material used in Analysis II. was made from the silver salt by the action of ethyl iodide.

I. 0.2193 grm. substance gave 0.2777 grm. AgBr.
II. 0.1497 grm. substance gave 0.1886 grm. AgBr.

| | Calculated for $(C_2H_5)C_5HBr_2O_3$. | Found. I. | II. |
|---|---|---|---|
| Br | 53.69 | 53.91 | 53.62 |

*βγ-Dibrompyromucamide,* $C_5HBr_2O_2NH_2$.— Since concentrated aqueous ammonia acted but slowly upon the ethyl βγ-dibrompyromucate in the cold, we heated the mixture in sealed tubes at 100° for several hours. The resulting amide we purified by recrystallization from dilute alcohol. It crystallized from alcohol in fine needles, which melted at 195–196°. It was readily soluble in alcohol, quite sparingly soluble in ether, chloroform, or benzol, and almost insoluble in carbonic disulphide or ligroin. Even in boiling water it was but sparingly soluble.

0.9791 grm. of substance gave 47.0 c.c. of moist nitrogen at 23° under a pressure of 739 mm.

| | Calculated for $C_5HBr_2O_2NH_2$. | Found. |
|---|---|---|
| N | 5.20 | 5.38 |

The $\beta\gamma$-dibrompyromucic acid appears to be incapable of forming an addition product with bromine. When the acid is exposed to an atmosphere of bromine at ordinary temperatures, hydrobromic acid is evolved, and tribrompyromucic acid is formed. This we identified by its melting-point, 218–219°, and by its other physical properties.

### *Action of Bromine and Water.*

Toennies obtained, by the action of bromine water upon the dibrompyromucic acid melting at 186°, a substance to which he assigned the formula $C_4H_2Br_2O_2$, and which he named dibromfumaric aldehyde. He published, however, in the preliminary paper to which we have already alluded,* no analysis of the substance. We have found that the action of aqueous bromine varies greatly, according to the conditions of the reaction; and although we have been able to prepare a substance whose properties nearly correspond to Toennies's description of the dibromfumaric aldehyde, we have not succeeded in making the yield satisfactory. If one molecule of bromine is slowly added by means of a current of air to the acid suspended in water, the color of the bromine gradually disappears, a part of the acid remains unaltered, while a part of it is converted into tetrabromfurfuran. After the solution had become colorless, we collected upon a filter the insoluble product, and washed it with a dilute solution of sodic carbonate. On acidifying the alkaline solution, the unaltered acid melting at 191° was precipitated. The solid insoluble in the solution of sodic carbonate dissolved readily in alcohol, and on cooling crystallized in long needles which melted at 64–65°, and gave on analysis the percentage of bromine required by tetrabromfurfuran.

0.2201 grm. substance gave 0.4319 grm. AgBr.

| | Calculated for $C_4Br_4O$. | Found. |
|---|---|---|
| Br | 83.33 | 83.52 |

A portion of the acid had therefore been decomposed according to the equation,

$$C_5H_2Br_2O_3 + 2\ Br_2 = C_4Br_4O + CO_2 + 2\ HBr.$$

From the aqueous solution which had been filtered from the tetrabromfurfuran and the unaltered acid we obtained by extraction with ether a small quantity of a substance which, when recrystallized from

* Berichte d. deutsch. chem. Gesellsch., xii. 1203.

dilute alcohol, melted at 89°. This gave on analysis a percentage of bromine which was approximately that required by the formula $C_4H_2Br_2O_2$.

0.1884 grm. substance gave 0.2897 grm. AgBr.

| | Calculated for $C_4H_2Br_2O_2$. | Found. |
|---|---|---|
| Br | 66.12 | 65.45 |

The formation of the tetrabromfurfuran could be avoided almost entirely by the rapid addition of the bromine. Still, rather more than one molecule of bromine was necessary for complete oxidation of the acid, and the purification of the product was difficult. The ethereal extract left on evaporation a viscous residue, which rarely solidified when allowed to stand in vacuo over sulphuric acid. By extracting this viscous residue with boiling water, we succeeded, however, in obtaining a crystalline product which melted at 90–91°, but which gave on analysis too low a percentage of bromine (I.). Since it seemed not improbable that the substance contained mucobromic acid, we dissolved it in a dilute solution of sodic carbonate, and extracted it from the alkaline solution with ether; but the percentage of bromine was unaltered (II.). By sublimation in a stream of carbonic dioxide, however, we obtained a product which melted at 89–90°, and gave the required percentage of bromine (III.).

I. 0.1496 grm. substance gave 0.2295 grm. AgBr.
II. 0.1981 grm. substance gave 0.2955 grm. AgBr.
III. 0.1340 grm. substance gave 0.2089 grm. AgBr.

| | Calculated for $C_4H_2Br_2O_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Br | 66.12 | 63.57 | 63.48 | 66.36 |

This substance is readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and crystallizes from aqueous solution in small prisms which often form lattice-like aggregations. By oxidation it yields mucobromic acid, and it must therefore be considered to be dibrommaleic aldehyde. The difficulty of its preparation in quantity made it impossible for us to study it more in detail at present, but we hope to return to it at some future time.

### *Action of Nitric Acid.*

Dilute nitric acid oxidizes the $\beta\gamma$-dibrompyromucic acid readily on heating. Carbonic dioxide is given off, and the solution then contains mucobromic and dibrommaleic acids. Toennies's erroneous statement that his acid was with difficulty oxidized even by strong nitric acid was doubtless due to the fact that but little hydrobromic acid is formed by the oxidation. For the complete oxidation of the acid we have found two parts of strong nitric acid (sp. gr. 1.42) diluted with five times its weight of water sufficient. After the reaction was over, we extracted with ether and treated the white crystalline residue left on evaporation of the ether with small quantities of cold water. The sparingly soluble mucobromic acid was thus left undissolved, and its identity proved by its melting-point (120–121°) and by analysis.

0.2040 grm. substance gave 0.2967 grm. AgBr.

| | Calculated for $C_4H_2Br_2O_3$. | Found. |
|---|---|---|
| Br | 62.02 | 61.90 |

The strongly acid aqueous solution was evaporated to dryness and the residue again treated with a small amount of cold water, in order to insure the removal of the mucobromic acid. The solution thus obtained was neutralized with baric carbonate, the barium salt precipitated with alcohol and recrystallized from water. The air-dried salt then proved to contain a percentage of barium, agreeing with that required by baric dibrommaleate.

0.5138 grm. of the air-dried salt gave on ignition with $H_2SO_4$ 0.2691 grm. $BaSO_4$.

| | Calculated for $BaC_4Br_2O_4 . 2\,H_2O$. | Found. |
|---|---|---|
| Ba | 30.78 | 30.80 |

The acid obtained from this barium salt was converted into its anhydride by sublimation, and its identity with dibrommaleic anhydride was shown by its melting-point, 114–115°.

The oxidation of $\beta\gamma$-dibrompyromucic acid with dilute nitric acid may therefore be expressed by the equations,

$$C_5H_2Br_2O_3 + 2\ O = C_4H_2Br_2O_3 + CO_2.$$
$$C_5H_2Br_2O_3 + 3\ O = C_4H_2Br_2O_4 + CO_2.$$

## Tribrompyromucic Acid.

Tribrompyromucic acid can readily be made from δ-monobrompyromucic tetrabromide by the action of an alcoholic solution of sodic hydrate. Although, as has already been remarked, this acid is formed through secondary reactions in the preparation of the dibrompyromucic acids from pyromucic tetrabromide, we have obtained in this way but a small quantity of the acid, and have prepared most of the material we have needed for the investigation from monobrompyromucic acid. The formation of the tribrompyromucic acid by the action of bromine upon the $\beta\gamma$-dibrompyromucic acid has already been noticed. Since the hydrogen of the isomeric dibrompyromucic acid cannot be directly replaced by bromine, tribrompyromucic acid cannot be made by the direct action of bromine upon pyromucic acid.

In the decomposition of the monobrompyromucic tetrabromide we have found a low temperature and a concentrated solution of sodic hydrate advantageous. The sodium salt of the tribrompyromucic acid is but sparingly soluble in alcohol, and may be separated by filtration. The alcoholic mother-liquors proved to contain a substance insoluble in water and readily volatile with the vapor of alcohol. For its isolation we precipitated the excess of sodic hydrate with carbonic dioxide, distilled the filtered solution, and precipitated the distillate by the addition of water. The heavy oil which was thus thrown down we dried with calcic chloride, and submitted it to fractional distillation in an atmosphere of carbonic dioxide under diminished pressure. After several distillations, by far the greater portion of the oil showed the constant boiling-point 96–98° under a pressure of 20 mm., and we were unable to isolate other definite products. An analysis showed the main product to be a tribromfurfuran.

0.3417 grm. substance gave 0.6299 AgBr.

| | Calculated for $C_4HBr_3O$. | Found. |
|---|---|---|
| Br | 78.68 | 78.39 |

Tribromfurfuran had, therefore, been formed from the monobrompyromucic tetrabromide according to the equation,

$$C_5H_3Br_5O_3 = C_4HBr_3O + CO_2 + 2\,HBr.$$

The sodium salt which had separated from the alcoholic solution we acidified with hydrochloric acid, and recrystallized the acid thus obtained from dilute alcohol, and finally from water.

I. 0.6837 grm. substance gave 0.4266 grm. $CO_2$ and 0.0221 grm. $H_2O$.
II. 0.1658 grm. substance gave 0.2684 grm. AgBr.
III. 0.1885 grm. substance gave 0.3047 grm. AgBr.

| | Calculated for $C_5HBr_3O_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 17.20 | 17.02 | | |
| H | 0.28 | 0.36 | | |
| Br | 68.77 | | 68.90 | 68.79 |

Tribrompyromucic acid crystallizes in minute clustered needles which melt at 218–219°. It is readily soluble in alcohol or ether, somewhat sparingly soluble in chloroform or benzol, and very sparingly soluble in carbonic disulphide or ligroin. It dissolves with difficulty even in boiling water, and the hot solution deposits the greater part of the acid on cooling. In order to determine the solubility of the acid in cold water, we boiled the saturated solution with baric carbonate and precipitated with sulphuric acid the barium dissolved.

I. 43.8259 grm. of a solution saturated at 19° gave 0.0105 grm. $BaSO_4$.
II. 42.6017 grm. of a solution saturated at 19° gave 0.0101 grm. $BaSO_4$.

According to these determinations the aqueous solution saturated at 19° contained the following percentages of the acid: —

| I. | II. |
|---|---|
| 0.072 | 0.071 |

*Baric Tribrompyromucate*, $Ba(C_5Br_3O_3)_2 . 3 H_2O$.—The barium salt we prepared by precipitating a solution of baric chloride with a solution of the acid in dilute ammonic hydrate and recrystallizing from boiling water the salt thus obtained. It crystallized in dendritic needles, which, when air-dried, contained three molecules of water, nearly all of which it lost over sulphuric acid.

I. 1.1629 grm. of the salt lost at 120° 0.0695 grm. $H_2O$.
II. 1.6160 grm. of the salt lost at 120° 0.0970 grm. $H_2O$.

| | Calculated for $Ba(C_5Br_3O_3)_2 . 3 H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 6.09 | 5.98 | 6.00 |

I. 0.6867 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1878 grm. $BaSO_4$.

II. 0.8009 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2192 grm. $BaSO_4$.

| | Calculated for $Ba(C_5Br_3O_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ba | 16.44 | 16.08 | 16.07 |

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 36.2176 grm. of a solution saturated at 20° gave 0.0197 grm. $BaSO_4$.
II. 32.6167 grm. of a solution saturated at 20° gave 0.0181 grm. $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 0.19 | 0.20 |

*Calcic Tribrompyromucate*, $Ca(C_5Br_3O_3)_2 . 4H_2O$. — The calcium salt we prepared by precipitating an ammoniacal solution of the acid with calcic chloride. When recrystallized from hot water, it formed clusters of fine dendritic needles, which were permanent in the air, but effloresced over sulphuric acid.

I. 1.5509 grm. of the salt lost at 120° 0.1385 grm. $H_2O$.
II. 0.9115 grm. of the salt lost at 120° 0.0799 grm. $H_2O$.

| | Calculated for $Ca(C_5Br_3O_3)_2 . 4 H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 8.91 | 8.93 | 8.77 |

I. 0.5885 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1060 grm. $CaSO_4$.
II. 0.6364 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1122 grm. $CaSO_4$.

| | Calculated for $Ca(C_5Br_3O_3)_2$. | Found. I. | II. |
|---|---|---|---|
| Ca | 5.44 | 5.30 | 5.18 |

In order to determine the solubility of the salt in cold water, we precipitated the saturated solution with ammonic oxalate, and converted the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

I. 34.5554 grm. of a solution saturated at 20° gave 0.0346 grm. $CaSO_4$.
II. 27.6386 grm. of a solution saturated at 20° gave 0.0267 grm. $CaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

| I. | II. |
|---|---|
| 0.54 | 0.57 |

*Argentic Tribrompyromucate*, $AgC_5Br_3O_3$. — Argentic nitrate gives even in the cold aqueous solution of the acid a crystalline precipitate of the silver salt, which is sparingly soluble even in boiling water. It may readily be prepared by precipitating a soluble salt of the acid with argentic nitrate and washing with hot water.

0.2977 grm. of the salt gave 0.1242 grm. AgBr.

| | Calculated for $AgC_5Br_3O_3$. | Found. |
|---|---|---|
| Ag | 23.68 | 23.96 |

*Sodic Tribrompyromucate*, $NaC_5Br_3O_3 . H_2O$. — The sodium salt we prepared by dissolving the acid in a dilute solution of sodic carbonate. The salt was not very soluble in cold water, and crystallized, on cooling the aqueous solution, in fine woolly needles, which contained one molecule of water and slowly effloresced over sulphuric acid.

I. 1.0434 grm. of the air-dried salt lost at 108° 0.0457 grm. $H_2O$.
II. 1.1171 grm. of the air-dried salt lost at 112° 0.0531 grm. $H_2O$.

| | Calculated for $NaC_5Br_3O_3 . H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 4.63 | 4.38 | 4.76 |

I. 0.5947 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1132 grm. $Na_2SO_4$.
II. 0.5036 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.0987 grm. $Na_2SO_4$.

| | Calculated for $NaC_5Br_3O_3$. | Found. I. | II. |
|---|---|---|---|
| Na | 6.20 | 6.17 | 6.35 |

*Potassic Tribrompyromucate*, $KC_5Br_3O_3 . H_2O$. — The potassium salt we prepared by neutralizing a dilute solution of potassic carbonate with the acid. It was not very soluble in cold water, and crystallized,

on cooling the aqueous solution, in globular aggregations of fine needles. The air-dried salt contained one molecule of water and slowly effloresced over sulphuric acid.

I. 1.6850 grm. of the air-dried salt lost at 120° 0.0753 grm. $H_2O$.
II. 1.7346 grm. of the air-dried salt lost at 112° 0.0784 grm. $H_2O$.

| | Calculated for $KC_5Br_3O_3 . H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 4.44 | 4.47 | 4.52 |

I. 0.6838 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1522 grm. $K_2SO_4$.
II. 0.5826 grm. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1319 grm. $K_2SO_4$.

| | Calculated for $KC_5Br_3O_3$. | Found. I. | II. |
|---|---|---|---|
| K | 10.10 | 10.09 | 10.16 |

*Ethyl Tribrompyromucate*, $(C_2H_5)C_5Br_3O_3$.— The ethyl ether we have prepared by warming the silver salt of the acid with ethyl iodide, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. In the latter case we found it convenient to use two parts of absolute alcohol and one part of concentrated sulphuric acid to one part of the acid. After heating for several hours at 100°, we precipitated the ether by the addition of water, washed it with a dilute solution of sodic carbonate, and recrystallized it from alcohol. It formed clear rectangular prisms, which melted at 104°, and have little or no odor at ordinary temperatures. It is readily soluble in ether, chloroform, benzol, or carbonic disulphide, somewhat more sparingly soluble in ligroin. It is quite sparingly soluble even in boiling alcohol. The material used in Analysis II. was made from the silver salt.

I. 0.1785 grm. substance gave 0.2677 grm. AgBr.
II. 0.1526 grm. substance gave 0.2284 grm. AgBr.

| | Calculated for $(C_2H_5)C_5Br_3O_3$. | Found. I. | II. |
|---|---|---|---|
| Br | 63.66 | 63.83 | 63.71 |

*Tribrompyromucamide*, $C_5Br_3O_2NH_2$. — Although ethyl tribrompyromucate is but slowly attacked by concentrated aqueous ammonia at ordinary temperatures, it is readily decomposed at 100° in sealed tube with the formation of tribrompyromucamide. The resulting product was purified by recrystallization from alcohol, and formed then fine

needles which melted at 222–223°. It was readily soluble in hot alcohol, quite sparingly soluble in ether, chloroform, or benzol, insoluble in carbonic disulphide or ligroin. It was nearly insoluble even in boiling water.

0.6792 grm. substance gave 23.5 c.c. of moist nitrogen at 22° and under a pressure of 744 mm.

| | Calculated for $C_5Br_3O_2NH_2$. | Found. |
|---|---|---|
| N | 4.02 | 3.92 |

### *Action of Bromine and Water.*

Bromine acts but slowly upon tribrompyromucic acid suspended in water, and even if the acid be finely subdivided a portion of it escapes decomposition. Since little action was visible when the vapor of bromine was slowly led in by means of a current of air, we added exactly one molecule of bromine, and then collected upon a filter the insoluble matter which remained. A portion of this dissolved in a dilute solution of sodic carbonate, and could be reprecipitated by the addition of hydrochloric acid. The properties of the precipitated acid and its melting-point (216°) showed it to be unaltered tribrompyromucic acid. The portion which was insoluble in the alkaline solution was dissolved in boiling alcohol, and on cooling crystallized in long slender needles which melted at 63–64°. An analysis gave the percentage of bromine required by tetrabromfurfuran.

0.2217 grm. substance gave 0.4359 grm. AgBr.

| | Calculated for $C_4Br_4O$. | Found. |
|---|---|---|
| Br | 83.33 | 83.68 |

The aqueous solution filtered from the tetrabromfurfuran and the unaltered tribrompyromucic acid yielded, on extraction with ether, dibrommaleic acid in quantity too small to admit of analysis, although its identity could readily be established by the melting-point of its anhydride (114–115°). With aqueous bromine, therefore, tribrompyromucic acid yields essentially tetrabromfurfuran and carbonic dioxide according to the equation,

$$C_5HBr_3O_3 + Br_2 = C_4Br_4O + CO_2 + HBr.$$

### *Action of Nitric Acid.*

Tribrompyromucic acid is much less readily attacked by dilute nitric acid than either of the dibrompyromucic acids, and to effect its oxida-

tion we were obliged to use three parts of strong nitric acid (sp. gr. 1.42) diluted with twice its weight of water to one part of the acid. After continued boiling the acid was dissolved, and from the clear solution, by extraction with ether, we were able to isolate only dibrommaleic acid, which melted at 125°, and gave by sublimation an anhydride which melted at 114–115°. The barium salt was prepared by neutralizing the acid in aqueous solution with baric carbonate, and precipitating the filtered solution with alcohol. This salt, when recrystallized from water and dried by exposure to the air, gave the percentage of barium required by baric dibrommaleate.

0.5259 grm. of the air-dried salt gave on ignition with $H_2SO_4$ 0.2765 grm. $BaSO_4$.

| | Calculated for $BaC_4Br_2O_4 . 2 H_2O$. | Found. |
|---|---|---|
| Ba | 30.78 | 30.91 |

By the oxidation of tribrompyromucic acid with nitric acid dibrommaleic acid is, therefore, formed according to the equation,

$$C_5HBr_3O_3 + 2\,O + H_2O = C_4H_2Br_2O_4 + CO_2 + HBr.$$

## Theoretical Considerations.

It is evident that definite conclusions as to the relative position of the bromine atoms in the various substituted pyromucic acids which we have described may be drawn from the products which result from the oxidation, and at the same time it seems to us that certain of our observations enable us to discriminate between the two structure formulæ for pyromucic acid which have hitherto seemed most probable. The behavior of pyromucic acid with phosphorus pentachloride, as shown by the experiments of Liès-Bodart,* or of its ethyl ether with acetyl chloride, as shown by Schmelz and Beilstein,† rendered it certain that pyromucic acid could not contain its third oxygen atom in the form of hydroxyl. Limpricht's ‡ experiments with furfuran (tetraphenol), and the indifference shown by pyromucic acid toward nascent hydrogen, excluded the possibility of the presence of an aldehyde or ketone group. The absence of both of these forms of oxygen has more recently been confirmed by the experiments of Odernheimer,§

* Ann. Chem. u. Pharm., c. 327.

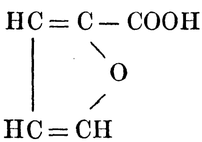
† Ibid., Suppl., iii. 276.

‡ Ibid., clxv. 282.

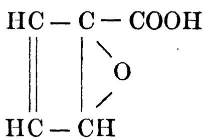
§ Ber. der deutsch. chem. Gesell., xvi. 2988.

who showed that pyromucic acid was not attacked by hydroxylamine, and of Wagner,* who failed to reduce the furfuran oxygen with zinc ethyl. Of the known forms in which oxygen occurs, therefore, there remains only the oxide form, C-O-C, which can be assumed to exist in the molecule of pyromucic acid. Moreover, Baeyer † has shown by the conversion of furfurol into furfuracrylic, furfurpropionic, furonic, and pimelic acids that the carboxyl group of the pyromucic acid is attached directly to one of these two carbon atoms which bear the oxygen atom.

In accordance with these facts, Baeyer has proposed the following three formulæ for pyromucic acid, the first of which he suggested in 1870,‡ the other two in 1877 §: —



1.



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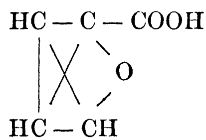
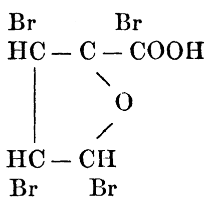


3.

Of these three formulæ, however, Baeyer preferred the second, since it appeared to explain most readily the formation from pyromucic acid of derivatives of fumaric acid which Limpricht had observed.

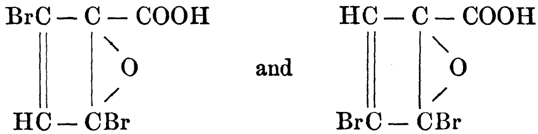
Since pyromucic acid forms an addition product containing four atoms of bromine, to this tetrabromide must be assigned in any case one and the same formula.



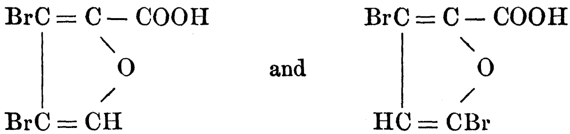
The simultaneous formation from this tetrabromide of two dibrompyromucic acids, which we have observed, one of which can be converted by oxidation into monobromfumaric (or monobrommaleic) acid, the second into dibrommaleic (or mucobromic) acid, seems to us to necessitate the rejection of the second formula. From the pyromucic

* Ber. der deutsch. chem. Gesell., xvii. 1967.
† Ibid., x. 1358. ‡ Ibid., iii. 517. § Ibid., x. 1361.

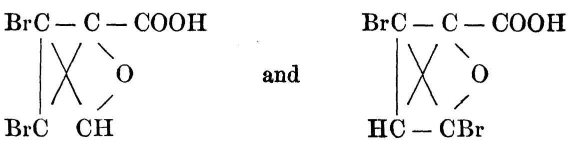
tetrabromide whose formula is given above two isomeric dibrompyromucic acids can in any case be formed; but if the second formula for pyromucic acid be adopted, these would necessarily have the structure,



both of which would yield on oxidation monobromfumaric or monobrommaleic acid. On the other hand, the adoption of either the first or the third formula for pyromucic acid would give for the resulting dibrompyromucic acids the forms,



or,

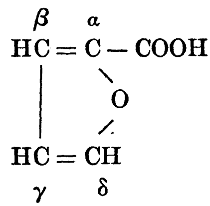


In either case, the oxidation products which we have observed would find in these formulæ a natural explanation.

While either of these two formulæ will explain the facts which we have observed, it seems to us that there can be no doubt that preference should be given to the first. Aside from the difficulty of explaining by means of the third formula the formation of the pyromucic tetrabromide, and the re-establishment of the carbon ties by the action of caustic alkalies, the formation of Heintzlemann's dehydromucic acid from mucic acid, which certainly is a dicarboxyfurfuran, would necessitate the assumption of a mode of dehydration in whose support, so far as we are aware, no analogous cases can be advanced. On the other hand, the ready formation of the lactones, as shown by the brilliant researches of Fittig, renders the formation of a stable oxide by the elimination of water involving hydroxyl groups attached to the first and fourth carbon atoms a matter in every way probable. We cannot deny that the adoption of the first formula renders the

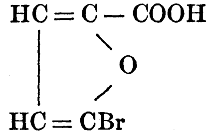
explanation of the formation of derivatives of fumaric or maleic acid by oxidation somewhat difficult (the same objection applies, of course, to a still greater degree to the third formula); and still we cannot consider this objection a serious one, while the normal behavior of substances containing the group C=C-C=C is not established, and the ease with which molecular rearrangements take place in non-saturated compounds is so well known. Until the structure of fumaric and maleic acids is more definitely established, it would be useless to attempt any discussion of the significance of the fact which we have established, that maleic acid and its derivatives, and not the corresponding derivatives of fumaric acid, are the first products formed in the decomposition of the substituted pyromucic acids.

If the carbon atoms in pyromucic acid are designated as usual, beginning with the carboxyl group,

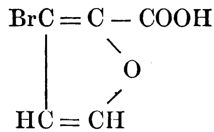


the constitution of the two isomeric dibrompyromucic acids may be expressed by the names which we have given to them, the $\beta\gamma$-dibrompyromucic acid (melting-point 191–192°), passing by oxidation into dibrommaleic acid, while the $\beta\delta$-dibrompyromucic acid yields monobrommaleic acid.

The determination of the constitution of the monobrompyromucic acids is a matter of no difficulty. The oxidation of the monobrompyromucic acid melting at 183–184° directly to maleic or fumaric acid shows that its bromine must be in the $\delta$-position, and its formula,

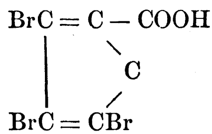


On the other hand, the monobrompyromucic acid melting at 128–129°, since it is formed by the reduction of either of the two dibrompyromucic acids, must have its bromine atom at $\beta$, and its formula is therefore



By oxidation with nitric acid it gives, as it should, monobromfumaric acid.

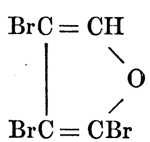
Since all the furfuran hydrogens are replaced by bromine in tribrompyromucic acid, but one form of the acid is possible, and that is



Of the substituted pyromucic acids which we have studied, those which contain a bromine atom in the $\delta$-position give, by oxidation with bromine water, dibasic acids, while those in which the $\delta$-hydrogen is not thus replaced yield ultimately the aldehyde acid, mucobromic acid. Although we are unable to follow at present the successive steps by which this oxidation proceeds, it may fairly be inferred that the $\alpha$-carbon atom is in any case completely oxidized, while the $\delta$-carbon atom appears in the aldehyde group whenever this is formed.

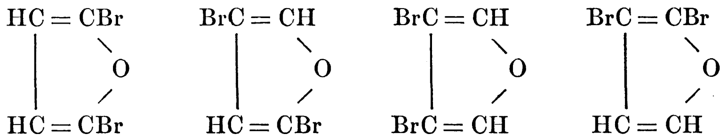
The strong analogies between the derivatives of furfuran and of benzol have frequently been pointed out during the past few years. It is interesting to note that by the action of bromine upon pyromucic acid the $\delta$ and $\beta$ hydrogen atoms are successively replaced. If the group CH=CH be substituted for the oxygen of furfuran, these become respectively the para and ortho positions of the aromatic series. While benzoic acid itself is converted into metabrombenzoic acid by the action of bromine, the formation of para and ortho derivatives under these conditions is more frequently observed in the aromatic series.

While we, unfortunately, have been able as yet to obtain no direct evidence as to the constitution of the substituted furfurans which we have described, there can be little doubt as to their structure. The tribromfurfuran obtained in the preparation of tribrompyromucic acid must certainly have the formula



and the tribromfurfuran obtained from the crude pyromucic tetrabromide is undoubtedly identical with it.

Of the four formulæ for dibromfurfuran, which are possible if the formulæ of furfuran we have adopted be correct,



1. 2. 3. 4.

the first undoubtedly represents the structure of a dibromfurfuran which has already been described in a preliminary paper by Mr. George T. Hartshorn and one of us.* The mode of its formation, and its reactions, leave no possible doubt as to its constitution. It seems to us that there can be no reasonable doubt that the two dibromfurfurans which we have just described must have the structure represented by the second and third formulæ, corresponding to the formulæ of the two dibrompyromucic acids formed at the same time. The latter formula, then, probably represents the more stable substance of lower boiling-point.

* Ber. der deutsch. chem. Gesell., xviii. 448